Anisotropic optical conductivity of the putative Kondo insulator $CeRu_4Sn_6$

V. Guritanu[1], P. Wissgott[2], T. Weig[3], H. Winkler[2], J. Sichelschmidt[1], M. Scheffler[3], A. Prokofiev[2], S. Kimura[4], T. Iizuka[4], A. M. Strydom[5], M. Dressel[3], F. Steglich[1], K. Held[2], and S. Paschen[2]

[1] *Max Planck Institute for Chemical Physics of Solids, 01187 Dresden, Germany*

[2] *Institute of Solid State Physics, Vienna University of Technology, Wiedner Hauptstr. 8-10, 1040 Vienna, Austria*

[3] *1. Physikalisches Institut, Universität Stuttgart, 70550 Stuttgart, Germany*

[4] *UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan and*

[5] *Physics Department, University of Johannesburg, Auckland Park 2006, South Africa*

(Dated: September 14, 2012)

Kondo insulators and in particular their non-cubic representatives have remained poorly understood. Here we report on the development of an anisotropic energy pseudogap in the tetragonal compound $CeRu_4Sn_6$ employing optical reflectivity measurements in broad frequency and temperature ranges, and local density approximation plus dynamical mean field theory calculations. The calculations provide evidence for a Kondo insulator-like response within the $a-a$ plane and a more metallic response along the c axis and qualitatively reproduce the experimental observations, helping to identify their origin.

Correlated materials with gapped or pseudo-gapped ground states continue to be of great interest. The gap in the electronic density of states (DOS) either opens gradually with decreasing temperature, as the pseudogap of high-temperature superconductors [1], or emerges at a continuous or first order phase transition [2–4]. In heavy fermion compounds [5] – systems in which f and conduction electrons strongly interact – a narrow hybridization gap is known to emerge gradually [6–9]. Generically, the Fermi energy is situated in one of the hybridized bands and a metallic heavy fermion ground state arises. Only for special cases the Fermi energy lies within the gap and the ground state is Kondo insulating. Metallic heavy fermion systems have been intensively investigated over the past decades and are now, at least away from quantum criticality [10], well understood [11] within the framework of Landau Fermi liquid theory. Hence, a very few parameters, most notably the effective mass, allow us to describe thermodynamic and transport properties at the lowest temperatures. In comparison, the physics of Kondo insulators has proven to be much less tractable. This is at least in part due to the fact that the gapped ground state inhibits a characterization via the above properties. Many experimental efforts have therefore focussed on the determination of the gap width from temperature dependencies, which has frequently led to conflicting results, in particular for anisotropic Kondo insulators such as CeNiSn [12]. Here the strongly anisotropic transport and magnetic properties have been interpreted phenomenologically on the basis of a V-shaped DOS [13] or by invoking a hybridization gap with nodes [14–16] or extrinsic effects such as impurities, off stoichiometry or strain [17, 18]. To advance the field it appears mandatory to model a number of carefully chosen materials *ab initio*, taking all essential ingredients into account.

Here we investigate a new material, $CeRu_4Sn_6$, which due to its tetragonal crystal structure is simpler than the previously studied orthorhombic materials. In a combined experimental and theoretical effort we provide direct spectroscopic evidence for the development of an anisotropic pseudogap: While weak metallicity prevails in the optical conductivity along the c axis, insulator-like behavior without a Drude peak is observed in the $a-a$ plane. We trace this back to a correlated band structure which is essentially gapped, except for the c direction, as shown by local density approximation (LDA) plus dynamical mean field theory (DMFT) calculations.

$CeRu_4Sn_6$ crystallizes in the tetragonal $I\bar{4}2m$ structure [19, 20], with $a = 6.8810$ Å and $c = 9.7520$ Å. Single crystals were grown from self flux, using the floating zone melting technique with optical heating [21]. Near-normal incidence reflectivity spectra on the *ac*-plane were measured using linearly polarized light, with the electric field $E \parallel a$ and $E \parallel c$, in a broad energy range from 0.5 meV to 30 eV. In the terahertz (THz) energy range ($0.5-5$ meV) a coherent-source spectrometer was used [22], for 5 meV-0.68 eV a Fourier transform spectrometer (Bruker IFS 66 v/S), with a reference gold layer evaporated *in situ* on the sample surface, for $0.6-1.25$ eV a JASCO FTIR 610 spectrometer with an Al mirror as reference, and for $1.2-30$ eV synchrotron radiation at the beamline 7B of UVSOR-II in Japan. Between 5 meV and 0.68 eV, a magnetic field of 7 T applied to polycrystalline $CeRu_4Sn_6$ did not change the reflectivity appreciably.

The theoretical optical conductivity was derived from DMFT combined with LDA within density functional theory [23, 24]. We performed a full-potential Wien2k [25] LDA calculation with spin-orbit coupling, and projected the Bloch waves onto maximally localized Wannier orbitals of Ce-4f, Ru-4d, and Sn-5p character [26, 27]. For this basis and a typical Coulomb repulsion of $U = 5.5$ eV for Ce [28], we included electronic correlations by DMFT, using quantum Monte Carlo simulations [29] for the $J = 5/2$ subset of the Ce-4f orbitals around the Fermi energy. The optical conductivity was calculated as described in Ref. 30, with an additional imaginary part of the self energy of 50 meV to account for impurity scattering and a minor readjustment of the chemicial potential by 50 meV due to different k-meshes employed.

As mentioned above, attempts to characterize Kondo

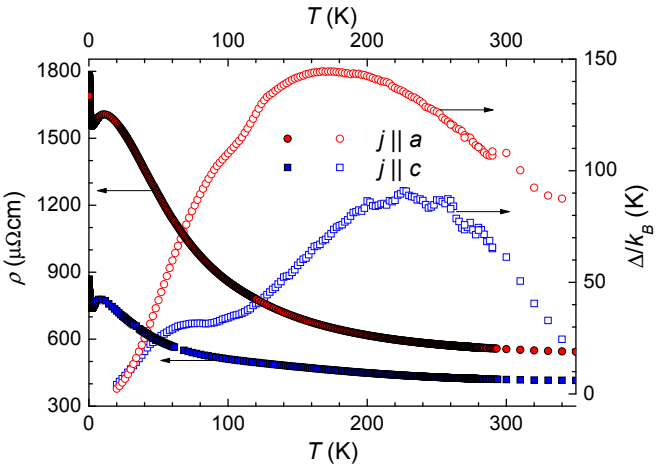

FIG. 1: (Color online) Temperature dependent electrical resistivity, $\rho(T)$ (left), and energy gap in units of temperature, Δ/k_B (right, see text), for single crystalline $CeRu_4Sn_6$, with the electrical current density j along the a and c axes.

insulators by a single, temperature-independent energy gap have generally failed. This is also the case for $CeRu_4Sn_6$, as illustrated by temperature-dependent electrical resistivity, $\rho(T)$, data along the two principal axes a and c (Fig. 1, left axis). As for other non-cubic systems (e.g., CeNiSn [31], U_2Ru_2Sn [32], $CeFe_2Al_{10}$ [33]), a pronounced anisotropy is observed. The temperature-dependent energy gaps $\Delta(T)$ for the two directions (Fig. 1, right axis) were obtained by fitting the $\rho(T)$ data in 20 K ranges with an Arrhenius law $\rho = \rho_0 \exp(\Delta/(2k_BT))$. Our results confirm that the definition of a unique energy gap scale characterizing the material seems arbitrary. Modeling temperature-dependent data with fine-structured (V-shaped or more complex) free electron bands yields improved fits [34], but provides little new insight. This clearly calls for a rethink of the problem and a novel approach, which is what we present here.

Optical spectroscopy is a powerful tool to characterize strongly correlated materials since the low energy scales in these systems can be ideally probed by optical excitations in the far infrared and THz frequency range. The optical reflectivity spectra, $R(\omega)$, of $CeRu_4Sn_6$ develop sizable temperature dependence at low energies (Fig. 2 a, b). This effect is larger for the a axis, in agreement with the steeper increase of the a-axis $\rho(T)$ with decreasing temperature (Fig. 1).

The frequency-dependent real part of the optical conductivity, $\sigma_1(\omega)$, was derived from the reflectivity data using a Kramers-Kronig fitting procedure [35, 36]. $\sigma_1(\omega)$ shows pronounced a-c anisotropy (Fig. 2 c-f), in particular at low temperatures. At 6 K, $\sigma_1(\omega)$ decreases continuously with decreasing frequency for the a axis. For the c axis a much more complex frequency dependence is observed: $\sigma_1(\omega)$ decreases down to 0.5 eV, passes over a local maximum at 120 meV and a local minimum at 30 meV, and increases with further decreasing frequency. At lowest frequencies, the optical conductivity is almost frequency independent for both polarizations and satisfying agreement with the dc values determined from $\rho(T)$ is found.

While the continuous depletion of spectral weight observed for the a axis with decreasing temperature (Fig. 2 e) is a feature of semiconductors, the upturn seen in $\sigma_1(\omega)$ below 30 meV for the c axis (Fig. 2 f) signals metallicity. Note, however, that $\sigma_1(\omega)$ for the a axis remains finite even at the lowest temperatures and frequencies, i.e. there is no fully developed energy gap. Thus we conclude that along the a and c axis $CeRu_4Sn_6$ behaves predominantly insulator- and metal-like, respectively.

The temperature evolution of the integrated spectral weight $N_{\rm eff}(\omega)$ for the a axis (Fig. 3 a) suggests that the pseudogap is due to strong correlations as opposed to band effects: The spectral weight lost at low temperatures and energies below 0.1 eV due to the pseudogap formation is still not fully recovered at 0.6 eV, as similarly seen in other Kondo insulators [37, 38]. Interestingly, this effect, though smaller, can also be discerned for the c axis (Fig. 3 b). This indicates that also there a remnant of a Kondo insulating gap exists.

The only other non-cubic Kondo insulator for which $\sigma_1(\omega)$ results along the different crystallographic directions are available is $CeFe_2Al_{10}$ [33]. Here a Drude-like feature appears for all three crystallographic directions; the anisotropy is thus much less pronounced than for $CeRu_4Sn_6$.

Can the salient features of $CeRu_4Sn_6$ be theoretically understood and if so on which level of approximation? To answer this question we performed, in a first step, LDA band structure calculations (Fig. 4 a). They yield a direct (but no indirect) bandgap of about 0.1 eV, separating Ru-4d and Sn-5p states below the Fermi level from Ce-4f states above it. The corresponding calculated $\sigma_1(\omega)$ is in strong disagreement with experiment (Fig. 4 b). In LDA+U, the 4f-states are split by the Coulomb repulsion U so that one electron is transferred from Ru-4d and Sn-5p to the Ce-4f orbital below the LDA+U Fermi level. Hence, part of the Ru- and Sn-states are now above the Fermi level (Fig. 4 c) and $CeRu_4Sn_6$ is predicted to be metallic in all directions (Fig. 4 d), again in contrast to experiment.

In a third step, LDA + DMFT calculations were performed at different temperatures. At high temperatures ($\sim$ 1000 K) the spectrum is similar to that of LDA+U (not shown). Upon reducing the temperature, we note the emergence of a Kondo resonance (red f-electron peak at the Fermi level in Fig. 5 a, c). This has dramatic consequences for $\sigma_1(\omega)$, which now shows good agreement with experiment (Fig. 5 b). Since the lowest experimental temperatures are not accessible in our theoretical approach, we mimic them by switching off the imaginary part of the self energy (Fig. 5 c). This turns out to further enhance the anisotropy. In particular, $\sigma_1(\omega)$ decreases sizably towards the lowest frequencies for the a axis while it levels out for the c axis (Fig. 5 d), thus correctly reproducing

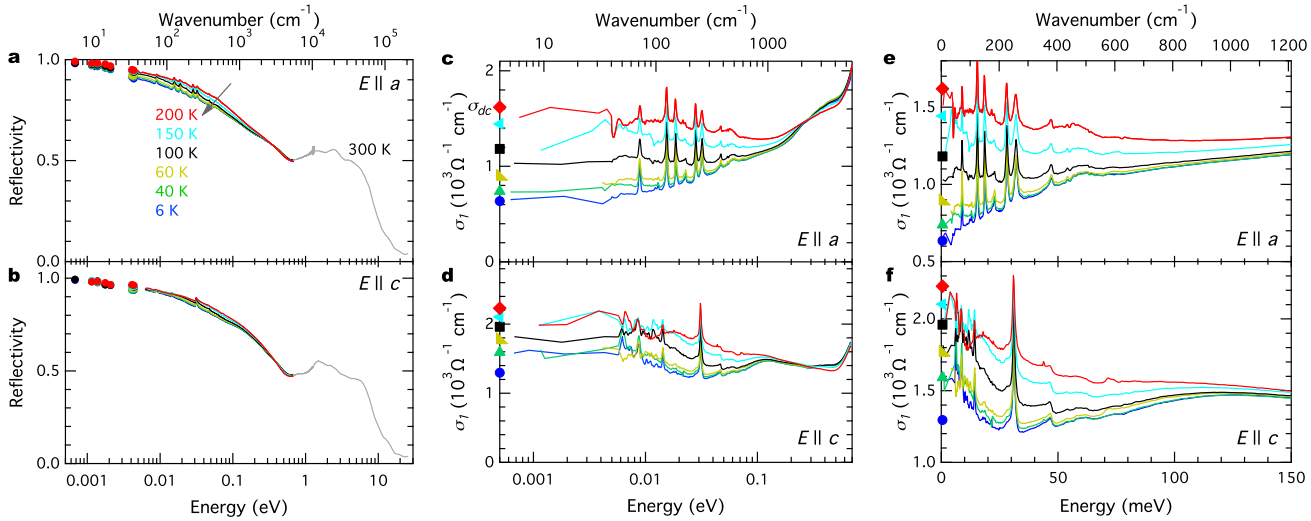

FIG. 2: (Color online) (a, b) Normal-incidence reflectivity spectra of single crystalline $CeRu_4Sn_6$ at various temperatures for $E \parallel a$ and $E \parallel c$, respectively. (c, d) Real parts of the optical conductivity, $\sigma_1(\omega)$, for $E \parallel a$ and $E \parallel c$, respectively. The filled circles on the vertical axis represent the independently measured dc conductivity data at the corresponding temperatures. (e, f) Low-energy part of $\sigma_1(\omega)$, showing, at the lowest temperatures, semiconductor-like behavior and weak metallicity for $E \parallel a$ and $E \parallel c$, respectively. The sharp features in (c, f) (at 8.9, 15.5, 18.6, 28, 31.6 meV along the a-axis, and at 8.7, 14.4, 30.9 meV along the c-axis) are phonon modes. They are temperature independent within our resolution ($2\,\mathrm{cm}^{-1} \equiv 0.25\,\mathrm{meV}$).

the experimental trends.

The k-resolved LDA+DMFT spectrum reveals the origin of the anisotropy. At 290 K, the Ce-4f states are strongly broadened (smearing of bands around the Fermi level, Fig. 5 e), which indicates the vicinity of the Kondo temperature where the scattering rate is high. At low temperatures, mimicked as above, the picture becomes clearer (Fig. 5 f): In large parts of the Brillouin zone there is a direct gap reminiscent of a Kondo insulator, particularly within the tetragonal $a-a$ plane, see e.g. $\Gamma \rightarrow (\frac{1}{2},\frac{1}{2},0)$. In contrast, in the c direction ($\Gamma \rightarrow X$) there is no such gap and the system is expected to show characteristics of a heavy fermion metal.

In summary, we have investigated the optical properties of single-crystalline $CeRu_4Sn_6$ by optical reflectivity measurements and LDA + DMFT calculations. The experimentally observed anisotropy is very pronounced, with metal-like features along one direction but semiconductor-like features elsewhere, and can be traced back to the peculiar k dependence of the correlated electron bands. The weak metallicity of $CeRu_4Sn_6$ is thus clearly a bulk effect and not due to topologically protected metallic surface states [39]. It will be most enlightening to see whether magnetic Ising anisotropy goes along with this peculiar quasiparticle anisotropy and whether any relation to "hastatic order" in URu_2Si_2 [40] can be established.

We thank M. Baenitz, M. Brando, A. Tóth, and A.

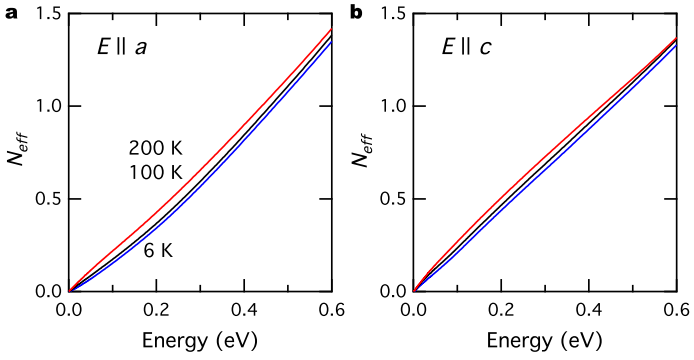

FIG. 3: (Color online) Integrated spectral weight of single-crystalline $CeRu_4Sn_6$ at 6, 100 and 200 K for $E \parallel a$ (a) and $E \parallel c$ (b).

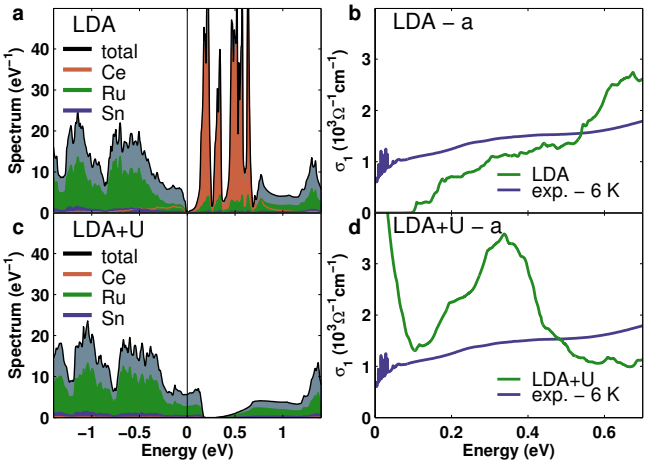

FIG. 4: (Color online) DOS and corresponding a-axis $\sigma_1(\omega)$ obtained by LDA (a, b) and LDA+U (c, d). The calculated c-axis conductivities are similar (not shown).

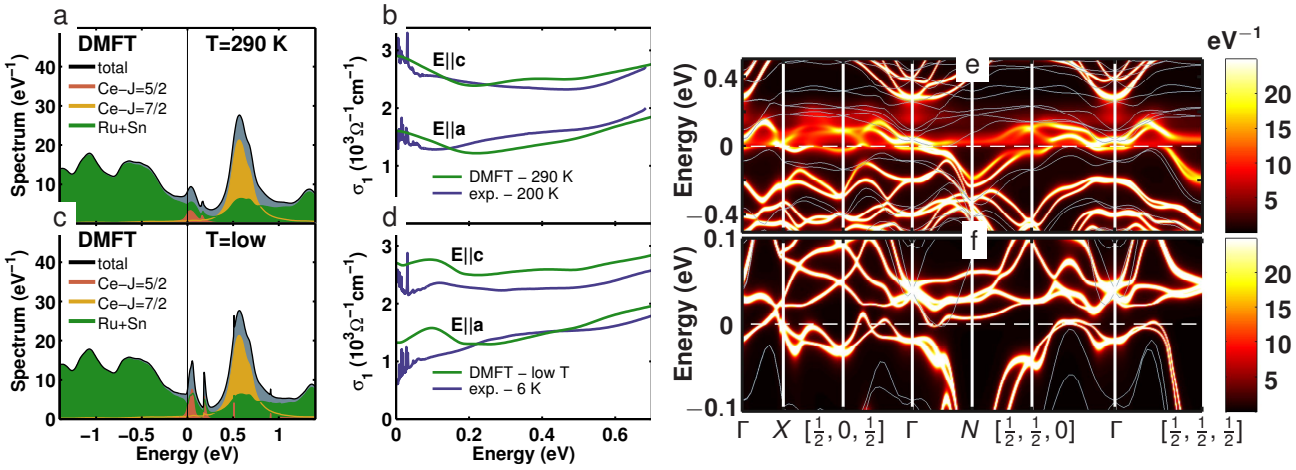

FIG. 5: (Color online) LDA+DMFT results: DOS at 290 K (a) and in the low temperature limit (c), and the corresponding optical conductivities (b, d; c axis conductivities shifted by $+10^3\Omega^{-1}\mathrm{cm}^{-1}$ for clarity) and k-resolved spectra (e, f; LDA band structure displayed as thin lines), showing a band crossing at the Fermi level for $\Gamma \to X$ (c axis) and a gap in the $a-a$ plane.

Pimenov for fruitful discussions, A. Irizawa for sharing beam time at UVSOR, and K. Imura for technical assistance. V.G. benefited from financial support from the Alexander von Humboldt Foundation, P.W. and K.H. from the Austrian Science Fund (FWF-SFB ViCoM F41), H.W., A.P. and S.P. from the FWF (project I623-N16) and the European Research Council (ERC advanced grant 227378), and A.M.S from the DFG(OE 511/1-1) and the Science Faculty of UJ. Calculations were done on the Vienna Scientific Cluster.

[1] H. Ding, T. Yokoya, J. C. Campuzano, T. Takahashi, M. Randeria, M. R. Norman, T. Mochiku, K. Kadowaki, and J. Giapintzakis, Nature **382**, 6586 (1996).
[2] C. de la Cruz, Q. Huang, J. W. Lynn, J. Li, W. Ratcliff, J. L. Zarestky, H. A. Mook, G. F. Chen, J. L. Luo, N. L. Wang, and P. Dai, Nature **453**, 899 (2008).
[3] O. Stockert, E. Faulhaber, G. Zwicknagl, N. Stüßer, H. S. Jeevan, M. Deppe, R. Borth, R. Küchler, M. Loewenhaupt, C. Geibel, and F. Steglich, Phys. Rev. Lett. **92**, 136401 (2004).
[4] A. R. Schmidt, M. H. Hamidian, P. Wahl, F. Meier, A. V. Balatsky, J. D. Garrett, T. J. Williams, G. M. Luke, and J. C. Davis, Nature **465**, 570 (2010).
[5] P. Coleman, in *Handbook of Magnetism and Advanced Magnetic Materials*, edited by H. Kronmüller and S. Parkin (John Wiley and Sons, West Sussex, UK, 2007), pp. 95–148.
[6] J. Levallois, F. Lévy-Bertrand, M. K. Tran, D. Stricker, J. A. Mydosh, Y.-K. Huang, and D. van der Marel, Phys. Rev. B **84**, 184420 (2011).
[7] W. K. Park, P. H. Tobash, F. Ronning, E. D. Bauer, J. L. Sarrao, J. D. Thompson, and L. H. Greene, Phys. Rev. Lett. **108**, 246403 (2012).
[8] F. F. Assaad, Phys. Rev. Lett. **83**, 796 (1999).
[9] J. Otsuki, H. Kusunose, and Y. Kuramoto, Phys. Rev. Lett. **102**, 017202 (2009).
[10] H. v. Löhneysen, A. Rosch, M. Vojta, and P. Wölfle, Rev. Mod. Phys. **79**, 1015 (2007).
[11] G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984).
[12] T. Takabatake, F. Teshima, H. Fujii, S. Nishigori, T. Suzuki, T. Fujita, Y. Yamaguchi, J. Sakurai, and D. Jaccard, Phys. Rev. B **41**, 9607 (1990).
[13] M. Kyogaku, Y. Kitaoka, H. Nakamura, K. Asayama, T. Takabatake, F. Teshima, and H. Fujii, J. Phys. Soc. Jpn. **59**, 1728 (1990).
[14] H. Ikeda and K. Miyake, J. Phys. Soc. Jpn. **65**, 1769 (1996).
[15] J. Moreno and P. Coleman, Phys. Rev. Lett. **84**, 342 (2000).
[16] T. Yamada and Y. Ōno, Phys. Rev. B **85**, 165114 (2012).
[17] T. Takabatake, G. Nakamoto, T. Yoshino, H. Fujii, K. Izawa, S. Nishigori, H. Goshima, T. Suzuki, T. Fujita, K. Maezawa, T. Hiraoka, Y. Okayama, I. Oguro, A. A. Menovsky, A. B. K. Neumaier, and K. Andres, Physica B **223&224**, 413 (1996).
[18] P. Schlottmann, Phys. Rev. B **46**, 998 (1992).
[19] G. Venturini, B. Chafik El Idrissi, J. F. Maréché and B. Malaman, Mater. Res. Bull. **25**, 1541 (1990).
[20] I. Das and E. V. Sampathkumaran, Phys. Rev. B **46**, 4250 (1992).
[21] A. Prokofiev and S. Paschen. Crystal Growth and Stoichiometry of Strongly Correlated Intermetallic Cerium Compounds, In: Modern Aspects of Bulk Crystal and Thin Film Preparation, 2012, Nikolai Kolesnikov and Elena Borisenko (Ed.), ISBN: 978-953-307-610-2, InTech.
[22] B. P. Gorshunov, A. A. Volkov, A. S. Prokhorov, I. E. Spektor, J. Akimitsu, M. Dressel, G. Nieuwenhuys, S. Tomic, and S. Uchida, Quantum Electron. **37**, 916 (2007).
[23] G. Kotliar, S. Y. Savrasov, K. Haule, V. S. Oudovenko,

O. Parcollet, and C. A. Marianetti, Rev. Mod. Phys. **78**, 865 (2006).
[24] K. Held, Adv. Phys. **56**, 829 (2007).
[25] P. Blaha, K. Schwarz, P. Sorantin, and S. B. Trickey, Comp. Phys. Comm. **59**, 399 (1990).
[26] J. Kunes, R. Arita, P. Wissgott, A. Toschi, H. Ikeda, and K. Held, Comp. Phys. Comm. **181**, 1888 (2010).
[27] A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, Comp. Phys. Comm. **178**, 685 (2008).
[28] A. K. McMahan, K. Held, and R. T. Scalettar, Phys. Rev. B **67**, 075108 (2003).
[29] J. E. Hirsch and R. M. Fye, Phys. Rev. Lett. **56**, 2521 (1986).
[30] P. Wissgott, J. Kunes, A. Toschi, and K. Held, Phys. Rev. B **85**, 205133 (2012).
[31] K.-i. Nakamura, Y. Kitaoka, K. Asayama, T. Takabatake, G. Nakamoto, H. Tanaka, and H. Fujii, Phys. Rev. B **53**, 6385 (1996).
[32] V. H. Tran, S. Paschen, A. Rabis, N. Senthilkumaran, M. Baenitz, F. Steglich, P. de V. du Plessis, and A. M. Strydom, Phys. Rev. B **67**, 075111 (2003).
[33] S. Kimura, Y. Muro, and T. Takabatake, J. Phys. Soc. Jpn. **80**, 033702 (2011).
[34] E. M. Brüning, M. Brando, M. Baenitz, A. Bentien, A. M. Strydom, R. E. Walstedt, and F. Steglich, Phys. Rev. B **82**, 125115 (2010).
[35] A. B. Kuzmenko, Rev. Sci. Instrum. **76**, 083108 (2005).
[36] In the THz frequency range $R(\omega)$ is very close to unity where small uncertainties in R can cause large errors in σ_1. Therefore, $\sigma_1(\omega)$ was obtained by a weighted average over finite frequency ranges.
[37] B. Bucher, Z. Schlesinger, P. C. Canfield, and Z. Fisk, Phys. Rev. Lett. **72**, 522 (1994).
[38] Z. Schlesinger, Z. Fisk, H.-T. Zhang, M. B. Maple, J. F. DiTusa, and G. Aeppli, Phys. Rev. Lett. **71**, 1748 (1993).
[39] M. Dzero, K. Sun, V. Galitski, and P. Coleman, Phys. Rev. Lett. **104**, 106408 (2010).
[40] P. Chandra, P. Coleman, and R. Flint, arXiv:1207.4828.